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Article

Abiotic Transformation of H_2 and CO_2 into Methane on a Natural Chromitite Rock

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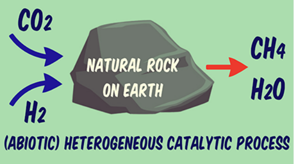
ABSTRACT: Understanding the origin and mechanism of the formation of methane from CO_2 is important because its formation would be related also to the origin of life on Earth. Both processes seem indissociable. To form methane, CO_2 is reduced to CO by hydrogen. The reduction of CO_2 might also correspond to the first step allowing the transition from CO_2 to organic molecules and then to the first block of life on Earth. In our experiments, we used a natural rock (chromitite) collected from an open mine. The major mineral phase naturally occurring in this sample is magnesiochromite (85−95%) with subordinate serpentine and chlorite (including Cr-bearing chlorite). For the first time, we provide an indisputable experimental proof of the (abiotic) formation of methane on a natural chromitite rock, without any previous pretreatment, in the presence of gaseous CO_2 and H_2 under low temperature and atmospheric pressure, which are the expected atmospheric environmental conditions that existed on Earth's crust when methane was formed in Nature. Methane is formed by a heterogeneous catalytic hydrogenation process at low temperature and atmospheric pressure. These results suggest that this transformation also goes on in other natural rocks existing on the surface of Earth, probably with higher efficacity. This means that natural rocks on Earth may contain catalytic sites and play the role of catalysts. The catalytic activity can be assigned to the presence of crystallographic phases and their surface composition, which promote the surface adsorption and transformation of gaseous reactants. The results demonstrate that a natural rock can activate, via heterogeneous catalysis, a very stable molecule such as CO_2. The literature demonstrates that N_2 can be also activated by the same process suggesting a coherent pathway to explain the formation of organic molecules and amino acids in Nature. *In situ* catalytic CO_2 hydrogenation in natural cavities should be considered as a realistic alternative method for CO_2 mitigation. It is supported that catalysis would play an important role in the formation of the first block of life on Earth.



KEYWORDS: *abiotic hydrogenation of CO_2, methanation, natural chromitite rock, heterogeneous catalysis, mechanism of the catalytic methanation, origin of life on Earth, activation of CO_2, formation of organic molecules and amino acids, CO_2 mitigation*

INTRODUCTION

Natural gas represents nearly one-quarter of the world's energy resources. The total worldwide proven reserves of natural gas were 198.8 trillion cubic meters (tcm) at the end of 2019 with a growth of about 16% in 10 years (170.5 tcm at the end of 2009). Methane is largely (>80%) the principal component of natural gas.[1] Besides the technological importance of methane,[2] increasing interest exists to understand the origin of methane because its formation would be related to the origin of life on Earth and assess its existence elsewhere in the Universe. To form methane, CO_2 is first reduced by hydrogen. There is a consensus that the reduction of CO_2 might correspond to the first step that allowed the transition from inorganic CO_2 to organic molecules and then to the first block of the origin of life on Earth.[3] All stages are processes that occurred under the conditions that existed on prebiotic Earth. A discussion exists about whether the reduction of CO_2 could be realized via an abiotic or biotic mechanism.[4,5]

Interest grows because mineral sites showing the presence of methane have been put in evidence in many places in the world. Previous works have reported, using molecular and isotopic analyses of liberated gas, that a natural rock hosts a considerable amount of adsorbed (abiotic) methane. It has been reported that serpentinization produces hydrogen, which by CO_2 reduction may lead to abiotic methane.[4−8]

Thermodynamics indicates that the hydrogenation of CO_2 into methane (Sabatier reaction) is an exothermic reaction ($CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$, $\Delta H° = -165$ kJ/mol), which is thermodynamically favored at low temperature and atmospheric conditions, i.e., conditions propitious for the beginning of life. However, there are competitive reactions that must be simultaneously considered, principally the decomposition of CO_2 ($CO_2 \leftrightarrow CO + 1/2O_2$, $\Delta H° = +293$ kJ/mol), carbon

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formation ($CO_2 + 2H_2 \leftrightarrow C + 2H_2O$, $\Delta H^\circ = -90$ kJ/mol), the reverse water–gas shift reaction ($CO_2 + H_2 \leftrightarrow CO + H_2O$, $\Delta H^\circ = +41$ kJ/mol), the methane water reforming ($CH_4 + H_2O \leftrightarrow CO + 3H_2$, $\Delta H^\circ =$ kJ/mol), the CO_2 reforming ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$, $\Delta H^\circ = +247$ kJ/mol), methanol formation ($CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$, $\Delta H^\circ = -91$ kJ/mol), and the formation of hydrocarbons by Fischer–Tropsch synthesis ($nCO + (2n + 1)H_2 \leftrightarrow C_nH_{2n+2} + nH_2O$). Then it can be expected that the formation of methane can be accompanied by the presence of secondary compounds. The reactional system considers exothermic and endothermic reactions. Therefore, to maximize the selectivity to methane, it is mandatory to select experiments at low reaction temperature minimizing secondary reactions. At a relatively low temperature (200–250 °C), the products are mainly CH_4 and H_2O. Increasing the temperature to above 450 °C results in an increase in the production of the CO by-product principally due to the reverse water–gas shift reaction. The CO_2 methanation process is favored at low reaction temperature, high pressure, and high H_2/CO_2 molar ratio. CO_2 methanation can be obtained with high equilibrium conversion between 25 and 400 °C. CO_2 methanation can reach a very high selectivity (near 100%). CO_2 conversion decreased with temperature but increased with the H_2/CO_2 ratio. At 250 °C, the conversion of CO_2 to CH_4 was almost complete at atmospheric pressure. At a H_2/CO_2 molar ratio of 4, the selectivity reached its maximum of almost 100%. Then, to determine the origin of methane, it is necessary to study the reaction minimizing all secondary reactions that can occur simultaneously with the formation of methane. However, despite that experimental reaction conditions are adequate to get a high conversion of CO_2 with high selectivity in methane, the major difficulty is the kinetic barrier of the different steps described in the pathway of the reaction of methanation. An adequate catalyst may improve the reaction rate of the rate-determining step, improving the global reaction rate. Reaction rate kinetics depends on the temperature, the reaction order, the partial pressure of each component, and the activation energy of the rate-determining step of the reaction pathway. The reaction order and the activation energy depend of the nature of the catalyst used to improve the kinetics of the reaction. To get experimentally high selectivity, it is necessary to perform the reaction in the presence of an adequate catalyst.[9−14]

Numerous attempts have been performed to elucidate the methanation reaction pathway. These include studies on laboratory-prepared catalysts and experiments employing *in situ*, transient, and *operando* techniques. Despite the enormous efforts paid, some mechanistic aspects remain unclear. The first step in the reaction mechanism of methanation of CO_2 is the direct dissociative adsorption of CO_2 ($CO_2 \rightarrow CO(ads) + O(ads)$) resulting in the formation of adsorbed CO(ads) and O(ads) on the metal surface followed by the hydrogenation of CO(ads) into methane. Direct dissociation has been reported by several groups over a variety of supported noble-metal-based catalysts. An alternative path suggests that CO_2 reacts with H(ads) species to form formate (COOH) via a reverse water–gas shift at the interface between the metal and the support (CO_2 + H(metal) → COOH(interface) → CO(metal) + OH(support)). The formate is then transformed to CO(ads) species, which are subsequently hydrogenated to methane. In some cases, the formation of CO(ads) is not accompanied by the concomitant apparition of formate species. On some supported metals (containing low concentration of OH groups), formate and carbonate species detected at the surface behave as side products and are not real intermediates. They are mainly spectators and have a minor influence on the reaction path. The adsorption of CO_2 occurs mainly on the support, whereas the adsorption and dissociation of H_2 take place on the metal surface. It is suggested that there is a migration of CO(ads) and H(ads) to the metal–support interface where the reaction takes place.[14−18] The dissociation of CO(ads) could proceed via a H-assisted path, probably by the formation of metal carbonyl hydride species. The dissociation of CO(ads) has been generally recognized as the rate-determining step of the reaction. In general, studies consider low pressure and temperatures <300 °C. Then it is logical to accept that the intermediate CO can transform further to more complex organic molecules. Catalysts with small metal nanoparticles have fewer active sites and bind CO species strongly, decreasing the available space for H(ads) species; hence, they have a lower overall activity. Catalysts with larger metal particles have more active sites, and CO is adsorbed weakly. This leads to more free space to accommodate H(ads) species, which can react with the CO(ads) and help its dissociation. Smaller particles present a lower amount of sites able to adsorb CO(ads) intermediates and thus fewer sites capable of performing the reaction. The morphologies (e.g., lateral planes) of large metal clusters permit more efficient hydrogen activation than small particles, which increases the rate of reaction.[19,20] Methanation of CO_2 proceeds via intermediate formation of adsorbed CO species produced by the reverse water–gas shift reaction, which are then hydrogenated to methane. The reactive surface intermediates could potentially be CO species linearly bonded on a reduced metal. The structure sensitivity of the reaction may be related to variation of the relative population of reactive surface intermediates (metal–CO).[21] CO_2 is a mildly acidic molecule, and it is attracted by basic sites of solid surfaces. Thus, CO_2 can be adsorbed on medium-strength basic sites to form covalent carbonates, hydrogen carbonates, and bidentate carbonates. Stronger basic sites lead to the formation of inactive carbonate species. These species are further reduced and hydrogenated by H atoms formed by dissociation of hydrogen at the surface of metal particles to form formates and then probably formaldehyde-type and methoxy species.[21,22]

Nevertheless, numerous studies concerning the formation of methane by hydrogenation of CO_2 have been achieved in laboratories, controlling the compositions and structures of synthetic catalysts during their preparation. To make our understanding of the origin of methane in Nature progressing, we now must perform studies using a natural rock instead of a synthetic catalyst, to have the elemental composition and crystal structure as they were during the formation of the natural rocks on Earth. It is a challenge to select a natural rock with adequate catalytic sites to perform the methanation of CO_2 with the desired activity and selectivity. Such experiments are necessary to strengthen our knowledge on the origin of methane and to understand the role of such natural rocks in the origin of life on Earth and maybe beyond.

Origin of Methane in Nature. A large discussion exists to define the exact origin of the different types of methane. In this context, methane presumably originates from two different processes. (a) Biotic methane is derived from biologically produced organic matter (by microbes (Archaea)). Methane is produced either by microbial or thermal decomposition of high-molecular-weight organic matter (kerogen). It is produced, in the absence of oxygen, underground in sedimentary rocks. (b) Abiotic (abiogenic) methane is formed from geological sources as raw materials. Abiotic chemical reactions do not include any organic matter. Methane is produced, in the absence of oxygen, from the reduction of carbon dioxide by hydrogen during fluid−rock interaction. The literature uses terms such as "microbial methane" (biogenic), which is formed through the microorganism-mediated decomposition of organic matter via acetate fermentation or reduction of CO_2, and "thermogenic methane", which is generated by degradation reactions of organic matter in deeper geological cavities under high pressure and temperature. In most geological environments, biotic and abiotic methanes are mixed, and despite the powerful analytical tools employed (molecular and isotopic methods), it is not easy to distinguish them. In fact, the chemical and isotopic fractionation occurring during gas migration and methane oxidation may hinder the isotopic and composition identification of methane sources.[4,5] Hence, there are unanswered questions about the origin of abiotic methane and how a natural terrestrial rock and its environment (gas or liquid) participated in the methanation pathways. This work aims to provide new arguments on the origin of methane in Earth.

Abiotic Formation of Methane in Natural Settings. There are several studies investigating the origin of abiotic and biotic methanes in different geological settings.[7,8,23−34] Research on olivine alteration shows that the formation of abiotic methane is influenced by traces of chromite and magnetite and other metal-rich minerals on the olivine surface, acting as catalysts. Methane formation is correlated with olivine dissolution at low temperatures.[23] Formation of abiotic methane and H_2 were detected during water−rock reactions using deionized water and N_2 on variably altered dunites (rock with >90% olivine). The formation of CH_4 occurred locally on the mineral surface rather than in aqueous solutions. The observed mineral phases were magnetite, chromite, and Ni-sulfides.[24] Studies on synthetic catalysts (Ru/TiO_2, Ru/Al_2O_3) with Ru equivalent to those occurring in chromitites in ophiolites or igneous complexes show that CH_4 is formed, at low temperature, via Sabatier reaction catalyzed by the Ru-phases.[25] Hydrothermally altered (serpentinization/olivine hydrolysis) peridotite (rock with olivine, orthopyroxene, clinopyroxene, and spinel) was studied using synthetic sea water analogous to the typical content of oceanic peridotites and synthetic olivine and chromite (spinel type). Abiotic CH_4 formation with a biogenic CH_4 component was observed. The authors concluded that CH_4 production was achieved through magnetite-catalyzed Fischer−Tropsch-type (FTT) synthesis processes and that magnetite is a better catalyst than chromite.[26] Experiments on serpentinization of natural olivine and orthopyroxene in water with and without H_2 indicate that abiotic synthesis of under water−rock reactions may be much more limited than other studies suggested, while the CH_4 measured may derive from background sources. The suspected catalysts are NiFe alloys (awaruite or others). The authors suggest that it is highly improbable that the CH_4 observed in the low-temperature experiments may have resulted from reduction of inorganic carbon. A separate gas phase may be more favorable for abiotic synthesis of CH_4.[8] While the formation of Ni-Fe-PGE (platinum group element) alloys from preexisting sulfides requires highly reducing conditions, the thermodynamic experiments on the stability of magnetite, heazlewoodite, bunsenite, and awaruite show that awaruite is stable in an extended range of fugacities fO_2, higher than previously considered. Thus, awaruite may be more common in serpentinites than originally thought, and it was suggested that abiotic methane may be stable in a wider range of redox conditions as well. The authors concluded that awaruite might catalyze the abiogenic synthesis of methane during serpentinization.[27] Studies on natural and synthetic komatiites (rare volcanic rocks with <45% SiO_2) indicate that Ni-sulfides (common phases in komatites) may be important catalysts for hydrothermal abiotic methanogenesis. These results were based on a 2 month experiment, reacting with an aqueous solution containing formic acid.[28] Reaction of non-altered natural peridotites in the presence of dissolved CO_2 and an Fe-Ni alloy catalyst reveals that H_2/CH_4 ratios cannot reliably discriminate abiotic from biotic methane.[29] A Monte Carlo simulation of the methanation reaction in either the bulk phase or for the bulk phase in equilibrium with a nanoporous silica was realized to determine the abiotic CO_2 methanation reaction during oceanic crust−seawater interactions (hydrothermal vents). High pressures and low temperatures favor the production of methane from CO_2. The reaction can be affected by the preferential adsorption of fluid in nanopores. Reaction conversions at equilibrium depend on nanopore size, nanopore chemistry, nanopore morphology, and some physical conditions. Results support the pathways for the abiotic organic synthesis.[30] Other studies on hydrothermal vent systems show that Cr_2O_3, in combination with Fe-bearing oxides, is an effective catalyst for abiotic synthesis of methane. The chromium component in ultramafic rocks could be an important factor for FTT synthesis during water−rock interaction in mid-ocean ridge hydrothermal systems. This could also help to account for the diverse communities of Archaea and Eubacteria inhabiting chimney deposits in the subsurface at deep-sea vents.[31] The origin of methane trapped in ophiolitic rocks (62 samples collected in 23 different locations) was analyzed via gas liberation during rock crushing. From the rocks analyzed, the chromitites with high concentrations of ruthenium host considerable amounts of methane with abiotic gas origin. Thus, Ru-minerals in chromitites may be key metal catalysts for methane production via Sabatier reaction.[6] Abiotic CH_4 is not formed directly in water or from magmatic sources or fluid inclusions. The most probable hypothesis is that CH_4 is formed at low temperature (<140 °C) via Sabatier reactions (CO_2 hydrogenation) in the gas phase by heterogeneous catalysis and is catalyzed by chromium and/or ruthenium-based minerals within metal-rich (catalyst) peridotites. CO is not a plausible geological source of CH_4. Microbial CH_4 generated under anaerobic, lower-temperature, aqueous conditions may be added as variable amounts of secondary gas.[32] Hydrothermally formed Ni-Fe alloy was shown to catalyze the formation of abiogenic CH_4 from dissolved bicarbonate under hydrothermal conditions. Methane is formed by an abiogenic process in the presence of the Ni_3Fe alloy as the catalyst under reducing conditions. In Nature, Ni_3Fe alloys form during hydrothermal alteration of olivine-rich rocks.[33] Sites with surface manifestations of methane in serpentinized peridotites (MSPs) are typically located between peridotites and carbonate-rich rocks (limestone, metasedimentary rocks). MSPs have principally an abiotic origin and is formed via FTT reaction between CO_2 (or other C compounds) and H_2 (from serpentinization) at low

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temperatures.[7] A mechanically activated reaction of olivine(Fe-Mg silicate) was used to produce abiotic light hydrocarbons. Mechanical treatment was performed on a mixture with acetone, deionized water, and a steel jar reactor. Experiments were conducted with water under a CO_2 atmosphere. Formation of methane can be attributed to serpentinization (including formation of magnetite-based minerals) and carbonation processes.[34]

These numerous and detailed studies of the literature allow concluding that the abiotic synthesis of methane would be a highly possible pathway explaining the formation of methane in Nature. Abiotic methane formation proceeds, very likely, via the reduction of inorganic carbon, following Sabatier catalytic processes suggesting that heterogeneous catalysis plays a primordial role in the abiotic transformation of CO_2 to methane. In addition, in these studies, many crystallographic phases observed in natural rocks were identified as responsible for the catalytic activity. The extensive literature in catalysis concerning the hydrogenation of CO_2 seems to support strongly this conclusion. Despite that the literature provided substantial experimental information concerning the abiotic formation of methane in several natural settings, we highlight that there is a lack of studies performed in both the presence of (i) gaseous CO_2 and H_2 as was probably present during methane formation on Earth and (ii) a natural rock occurring in the original settings where methane was formed. Another important observation is that previous studies have been performed selecting contrastingly different reaction conditions, which are not comparable among the settings where methane is expected to be formed (e.g., ocean-floor, hydrothermal vents, on-land), particularly (i) using synthetic solids in place of the natural mineral, (ii) using synthetic aqueous solution of dissolved CO_2 ($CO_{2(aq)}$ + HCO_3^- and CO_3[2]) as the carbon source, (iii) adding synthetic salt (NaCl) to the aqueous solution to simulate salinity of the solution, or deionized or ultrapure water or formic acid, or (iv) washing the natural minerals with different solvents, using buffer solutions to fix the pH of the solutions, modifying the initial natural rock (drastically in mechanical mixing or using solvents), and the physicochemical properties of natural mineral assemblages. This is a serious drawback limiting the scientific impact of the current literature results in understanding the origin of methane. It is well known that experimental reaction conditions (liquid and/or gas) could modify drastically the catalytic activity of a catalyst. Because the abiotic transformation of CO_2 is realized by a catalytic process, the surface of the natural catalysts (the locus of the catalytic reaction) must be studied in detail. In addition, the catalytic performance must be correlated with the state of the catalyst during the reaction and not only with the state of the catalyst before the experiment as the catalyst can be modified during the catalytic reaction. We remark that a very small amount of component at the surface of the natural rock might modify drastically the catalytic activity of the solid (catalyst). Finally, in previous studies, concerning the origin of methane, there is an absence of the influence of mass transfer and diffusional processes. More precisely, none of these studies refer to these processes. This is an important drawback because these processes limit the experimental reaction rate of methanation. Experiments need to eliminate the effect of these processes; otherwise, the result obtained is not the rate of reaction on the surface of the catalyst but the rate of transfer of the reactant from the bulk of the phases and/or the rate limited by the rate of diffusion of the reactants or products inside the pores of the solid. Consequently, this limits the adequacy of the catalytic activity interpretations and the comparison between different studies. The conclusion is that well-documented results presented in the literature give several important and valuable arguments to support the abiotic formation of methane in various terrestrial settings. However, there are no experiments employing both rocks in their natural state (representing the conditions existed in geological settings when methane was formed) and the influence of gaseous reactants, CO_2 and H_2 (simulating the actual Sabatier reaction). Then it can be concluded that, presently, there are no results proving unquestionably that abiotic methane was formed from gaseous CO_2 and H_2 in contact within a natural rock, in a terrestrial setting.

These limitations in the current literature confirm the importance of our work. Our objective is to advance the understanding of the origin of methane on Earth. Hence, it is necessary (i) to investigate the abiotic catalytic formation of methane under the same reaction conditions (using the natural rock and environmental reaction conditions (gaseous H_2 and CO_2)) expected to occur in Nature when methane was formed, (ii) to study the physicochemical transformation of the rock during the catalytic reaction, (iii) to correlate the catalytic performances with the real state of the rock during reaction, and (iv) to verify that the study is realized in the absence of mass transfer and diffusional limitations.

In this work, we provide a complete experimental design using natural chromitite rock, avoiding carefully any modification of its natural state prior to the experiment. For the first time, we demonstrate that a natural rock contains the necessary catalytic sites able to perform the (abiotic) catalytic hydrogenation of CO_2 into methane under the reaction conditions expected to have occurred in Nature when methane was formed. The natural chromitite rock was used as our catalyst (S-1). It was collected from an open mine in Greece. Chromitites are rocks occurring in ultramafic sequences (peridotites) and include dominantly (>90%) one or more minerals of the spinel supergroup (Al- or Cr-spinel, magnesiochromite, chromite, etc.). It was experimentally determined that chromitite hosts adsorbed methane,[4−6] and it was concluded that it participated in the formation of methane present in geological settings where it outcrops.

Catalytic tests were carried out in a fixed-bed tubular reactor at atmospheric pressure (S-2). The evolution of the activity and stability of a nonthermally or chemically treated chromitite was studied feeding CO_2 and H_2 (or only CO_2) at atmospheric reaction conditions with increasing temperature. The reaction conditions selected in this study, gaseous H_2 and CO_2, atmospheric pressure, and low temperature, probably correspond to the conditions of the natural setting (on-land serpentinization) where the adsorbed methane was formed. As an attempt to explain the catalytic transformation of CO_2 into methane, the chromitite was characterized (before and after the catalytic test) by several physicochemical methods examining the bulk composition and the surface of the rock grains. The catalytic properties of the rock were related with the catalytic performances. Mass transfer and diffusional limitation studies were also performed (S-3). Blank tests were also realized in order to verify the absence of methane (or other compounds) background in the measurements.

Table 1. Catalytic Activity of Natural Chromitite Rock Performed at Atmospheric Pressure[a]

test	stage	treatment conditions	average methane production measured in 1 hour (µmoles)			
			150 °C	200 °C	300 °C	350 °C
Test Nº1	1	heat up to 350°C, in $CO_2/H_2/He$				
	1	cool down to 50°C in He				
	2	heat up to 300°C, in $CO_2/H_2/He$	0	0.18	2.98	–
Test Nº2	1	heat up to 350°C in He				
	2	flow switch to $CO_2/H_2/He$ for 20 h, at 350°C	–	–	–	3.89
	2	flow switch to H_2/He for 1h, at 350°C				
	2	flow switch to $CO_2/H_2/He$, at 350°C				
	3	cool down to 200°C in $CO_2/H_2/He$				
Test Nº3	1	reduction at 200°C in H_2, for 2 h				
	1	cool down to 50°C in H_2				
	2	heat up to 200°C, in $CO_2/H_2/He$	0.28	3.00	–	–

[a] Fixed-bed reactors (ID = 4 mm, 200 mg (200−315 μm)) were used (S-2). Experimental reaction conditions (S-2) of the catalytic tests and average amount of CH_4 produced in 1 h, in the presence of $CO_2/H_2/He$, at the second stage of each test. At the beginning of each test, a fresh "non-used" rock sample was loaded in the reactor and kept until the end of the test (S-2). Experimental and theoretical methods to estimate the magnitude of diffusional limitations in fixed-bed reactors were used to verify if the reaction rate is kinetically controlled (S-3).

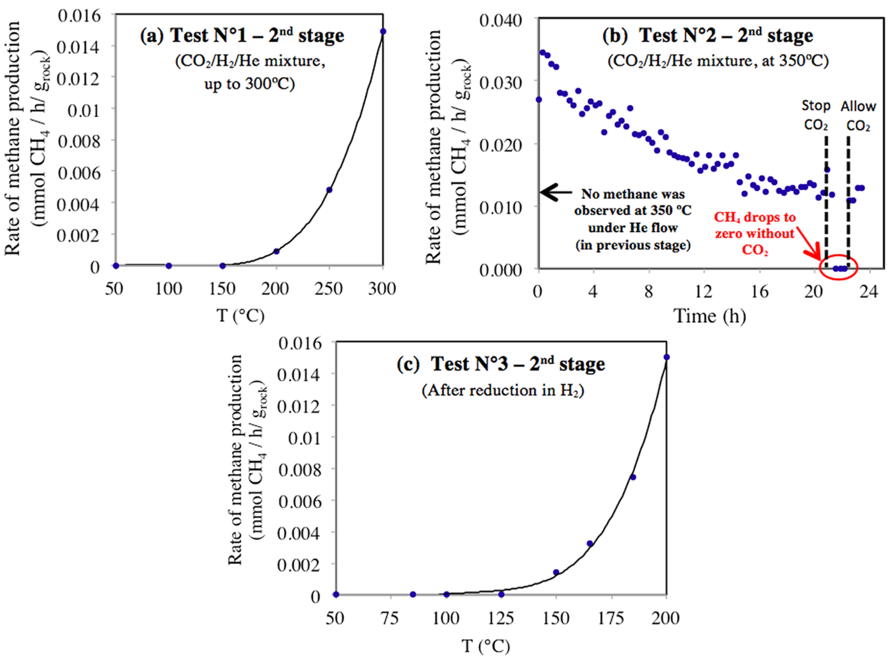

Figure 1. Catalytic activity of the natural chromitite rock (S-2). (a) Test N°1 − second stage, performed at standard reaction conditions (CO_2 (10 vol %)/H_2 (40 vol %)/He, 20 mL/min, 1 atm), using a rock sample previously heated up to 350 °C under standard reaction conditions; (b) Test N°2 − second stage, performed at standard reaction conditions and 350 °C, using a rock sample previously heated up to 350 °C in He flow. The CO_2 flow is stopped after 20 h of reaction and readmitted after 1 h; (c) Test N°3 − second stage, performed at standard reaction conditions with a rock sample previously reduced in H_2, at 200 °C for 2 h (S-2).

■ RESULTS

The Catalytic Activity of the Natural Chromitite Rock.

The reaction can be considered to completely take place in a full kinetic regime, while the mass transfer criteria are fully satisfied (S-3). It is important to clarify that the study did not aim to quantify the catalytic activity of the rock, but rather to show that it can catalyze the methanation reaction, under the conditions encountered in Nature. In this context, the calculations provided on methane production are given for comparative purposes only to support and enrich the qualitative discussion. The maximum amount of methane is given by the thermodynamic equilibrium, as dictated by the reaction conditions. For a feed gas mixture of CO_2 (10 vol %) and H_2 (40 vol %) diluted in He, temperatures in the range 50−300 °C, and atmospheric pressure, the molar percentage of methane at the equilibrium is about 12%. A blank test without the chromitite was performed under standard reaction conditions, showing the absence of methane formed in the absence of chromitite. Data are, of course, valid under the conditions and restrictions of the experimental tests performed. Three tests (Tests N°1, 2, and 3, Table 1) were performed to study the catalytic activity (S-3). Three aliquots of the fresh pulverized chromitite were prepared. The first aliquot was tested in Test N°1 without any chemical or temperature pretreatment. In the first stage, a gas mixture (20 mL/min) of CO_2 (10 vol %) and H_2 (40 vol %) diluted in He, from now on called "the standard $CO_2/H_2/He$ gas mixture", was admitted into the reactor containing the fresh chromitite, and the temperature was increased until 350 °C. CH_4 was only observed at 350 °C (not shown). Then, the reactor was cooled down to 50 °C under He. No methane was detected at temperatures below 350 °C. The first stage of Test 1 was mostly exploratory. The purpose was not to evaluate methane production but to find out whether the "as received" rock would show any activity when exposed to CO_2 and H_2, at relatively low temperatures. As no methane was detected at room temperature, the analysis was performed at a slightly higher temperature, and methane was again not produced. Temperature was further increased, and a sequence of analysis was run until methane was finally detected at 350 °C. This sequence means that there is neither desorption of methane initially adsorbed on or absorbed in the rock nor methane production via homogeneous reaction of CO_2 and H_2 below 350 °C.

In the second stage, as soon as the reactor was cooled down to 50 °C (after the first stage), the standard $CO_2/H_2/He$ gas mixture was admitted again, and the temperature was increased up to 300 °C (Figure 1a). Methane is now detected at 200 °C (about 0.0009 $mmolCH_4/h/g_{rock}$), confirming that catalytic sites were activated on the rock during the reaction conditions of methanation applied in the first stage. The rate of methane production increases drastically as the temperature increases. At 300 °C, the reaction rate (0.015 $mmolCH_4/h/g_{rock}$) is like the one obtained in the first stage of the experiment at 350 °C for the non-pretreated chromitite. Results clearly show that the nontreated, fresh chromitite can catalyze the production of methane from gaseous CO_2 and H_2 by heterogeneous catalysis. The chromitite reaches a measurable catalytic activity at low temperatures (<200 °C), after being exposed to CO_2 and H_2 at higher temperatures. Results suggest that methane is already formed at lower temperatures (<175 °C), probably in amounts under the detection limit. Thermodynamics indicate that methane can be formed at room temperature,[9−12] and it would be expected that increasing the contact time (by decreasing spatial velocity) would allow detecting methane formation at significantly lower temperature. The whole test was run on the same sample, without removing it in between the stages, and therefore, no analysis was performed to directly prove the presence of activated sites at the rock surface, before stage 2. However, the formation of methane starting from lower temperatures in stage 2, under the same gas flow, indirectly proves the activation of sites. The small amounts of CO detected are attributed to the occurrence the reverse water−gas shift reaction, which is always present simultaneously with the methanation reactions. These results were not included as they were not relevant to the focus of the discussion.

In the Test N°2 (Table 1), the *in situ* (i.e., inside the reactor) activation, along with the exposure to CO_2 and H_2, of catalytic sites in the chromitite was further studied. Therefore, the second aliquot was placed in the reactor and heated up to 350 °C under He flow (first stage). There was no detectable release (previously adsorbed on or absorbed in the chromitite) or formation of CH_4, CO_2, and H_2. In the second stage, the standard $CO_2/H_2/He$ gas mixture was admitted at 350 °C, and methane was immediately detected. The rate of methane production decreased from around 0.03 to 0.014 $mmolCH_4/h/g_{rock}$, after 20 h of reaction (Figure 1b). After stopping CO_2 flow, methane production dropped to zero, meaning that this gas is not produced when the rock is only exposed to H_2/He flow. After about 50 min, CO_2 flow was admitted again, and the production of methane was brought back to the same rate as before stopping CO_2 flow (Figure 1b). This is an unquestionable experimental proof that (i) there is no desorption of methane, CO_2, or H_2, eventually adsorbed on or absorbed in the fresh rock sample; (ii) active catalytic sites are created at the chromitite surface upon exposure to CO_2 and H_2; and (iii) methane is only produced at the activated mineral surfaces, in the presence of both CO_2 and H_2 gases, via a heterogeneous catalytic process.

The third aliquot was introduced in the reactor to perform Test N°3. The catalytic performance of the chromitite was studied after reduction with hydrogen. In the first stage, the chromitite was reduced at 200 °C under hydrogen flow and then was cooled down to 50 °C. In the second stage, the rock was heated up only to 200 °C, under the standard $CO_2/H_2/He$ gas mixture. Measurements were taken under stable rates of methane production, after steady-state conditions are reached and before deactivation starts occurring. Methane is detected starting from 150 °C (0.0014 $mmolCH_4/h/g_{rock}$), although its incipient formation very probably starts at lower temperatures (∼125 °C). At 200 °C, the rate of methane production (0.015 $mmolCH_4/h/g_{rock}$) is about 15 times the rate reached after activation (Test N°1), in the presence of CO_2 and H_2, at the same temperature (Figure 1c). Results show that the hydrogen reduction pretreatment allows an effective catalytic activation of the natural rock, leading to a higher catalytic activity than the activation in the presence of CO_2 and H_2, where the presence of CO_2 probably inhibits the reduction of the chromitite. This is clearly observed in Table 1, showing the average amount of methane produced in 1 h, after different pretreatments of the chromitite. The important conclusion is that the chromitite, which is collected from an open pit mine, can catalyze (via an abiotic process) methane production in the presence of gaseous CO_2 and H_2, at low temperature (∼125 °C) and atmospheric pressure conditions. If the same experiments were performed in a batch reactor (long residence time (months, years)), certainly methane would be observed approximately at room temperature. The principal conclusion of these results is that natural oxides and other compounds comprising the chromitite are able to promote the heterogeneous catalytic hydrogenation of CO_2 in natural geological cavities, explaining the abiotic origin of natural gas on Earth.

The Bulk State of Chromitite Rock. ICP-AES (S-4) and XRF (S-5) analyses of the chromitite bulk composition are in good agreement, with differences within the range of experimental errors (Table 2). A relevant result is that none

Table 2. Composition of the Natural Chromitite Rock Sample (without any Treatment) Obtained by ICP-AES (S-4) and XRF (S-5), Values in Parentheses[a]

component	wt %	component	wt %	component	wt %
Cr	28.2 (29.1)	Ni	0.2 (0.1)	Zn	0.03
Al	10.5 (9.5)	Mn	0.2	Cu	0.02
Fe	10.1 (10.0)	Ti	0.05 (0.04)	Cl	0.07
Mg	10.0 (9.4)	Co	0.02	S	0.03
Si	1.8 (1.4)	V	0.1		

[a] ICP-AES detection limits are Pd and Li (below 50 mg/kg); Rh, Ru, K, Sr (below 100 mg/kg); and Ba, Ca, P (below 200 mg/kg). For XRF, the detection limit of a given element is 0.1%.

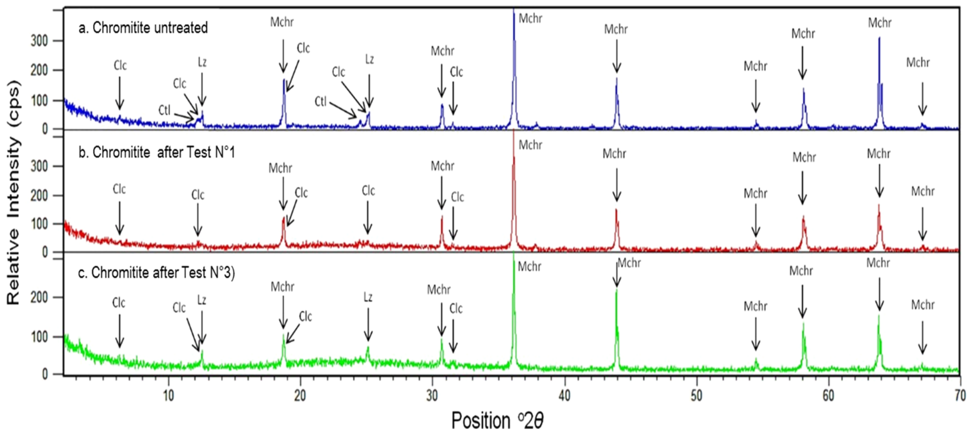

Figure 2. Petrographic description. X-ray diffraction patterns (XRD2) of the natural chromitite rock (a) and the natural chromitite rock after Tests N°1 (b) and N°3 (c). Mchr: magnesiochromite, Clc: clinochlore, Lz: lizardite, and Ctl: chrysotile.

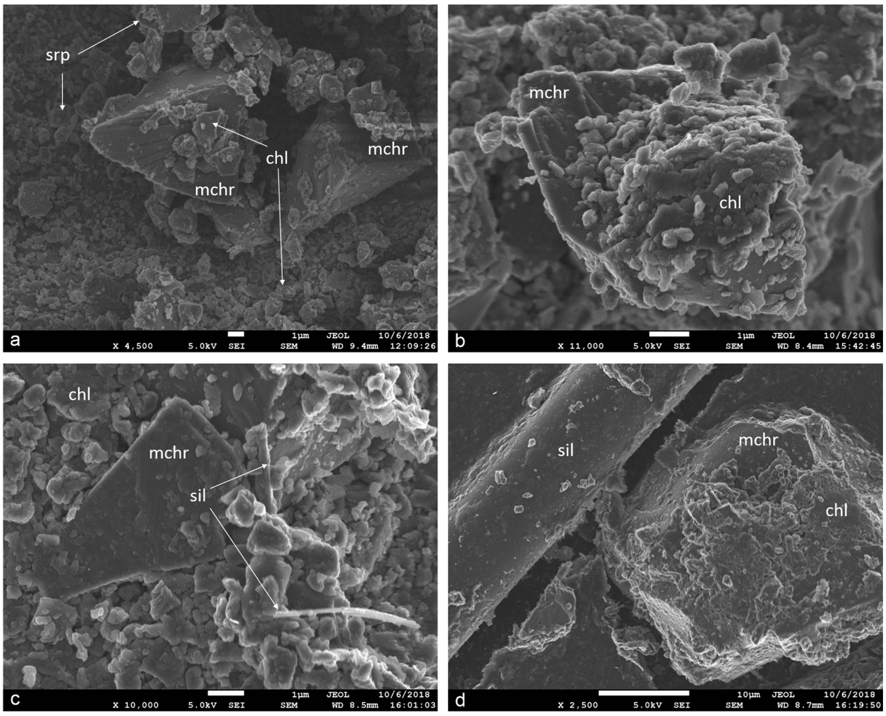

Figure 3. Petrographic description (S-7). Secondary electron images of (a) the pulverized natural chromitite rock and (b, c) the pulverized natural chromitite rock after Test N°1 and (d) after Test N°3. The mixture is dominated by magnesiochromite (mchr), less chlorite (chl), and rare serpentine (srp). Silica (sil) nano- to microfibers and rods appear after Test N°1 and Test N°3.

of the most active metals reported for methanation reaction (Ru, Rh, Pd)[9−21] are present (at least in detectable amounts), in the tested aliquots of the chromitite sample. In general, chromitites are expected to have about less than 300 ppb total PME with a highly heterogeneous distribution in the chromitite host.[4,6,7]

A combination of crystallographic analysis (XRD, S-6), optical microscopy and SEM (S-7), and ICP chemical analyses

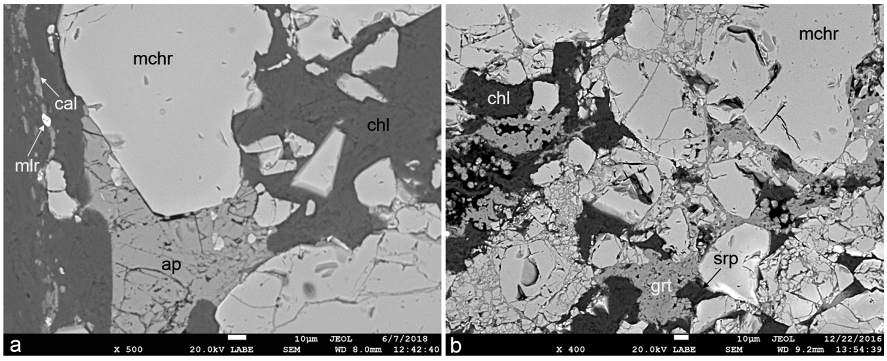

Figure 4. Petrographic description (S-7). Backscattered electron images of the natural chromitite rock: (a) magnesiochromite (mchr) crystals with accessory apatite (ap) and interstitial, secondary chlorite (chl), millerite (mlr), and calcite (cal); (b) cataclastic magnesiochromite with interstitial chlorite, serpentine (spr), and garnet (grt).

(S-4) was performed to understand the mineralogical composition of the chromitite as the mineral distribution in natural rocks is highly heterogeneous. The X-ray diffraction patterns of the chromitite aliquots were determined independently with two different analyzers (S-6). The XRD1 diffractogram of the fresh chromitite reveals a typical spinel structure (cubic symmetry, space group *Fd-3m*) as the major phase. To index the principal reflections of the diffractogram, it was compared with a pure synthetic magnesiochromite pattern (ideal formula $MgCr_2O_4$). However, an important shift of all reflections toward higher angles was observed, indicating a contraction of the lattice parameter and suggesting a modification of its crystal structure. A previous study related to the crystal chemistry of detrital chromian spinel showed that the lattice parameter and the oxygen positional parameter can differ depending on the elemental composition of the octahedra and tetrahedra of the crystal structure. Therefore, we suggest that Mg and Cr have been partially substituted by mainly Al and Fe and by other elements of the above reported ICP (S-4) and XRF (S-5) analyses. Additionally, the XRD1 (S-6) analysis pointed lizardite ($Mg_3(Si_2O_5)(OH)_4$) and clinochlore ($((Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8)$ as minor phases.[8] Moreover, a semiquantification based on the intensity of the main reflections of the different phases led to the following composition: magnesiochromite 90%, lizardite 8%, and clinochlore 2%.

From XRD2 (Figure 2), magnesiochromite is the dominant phase followed by less clinochlore (ideal formula: $(Mg,Fe)_5Al(Si_3Al)O_{10}(OH)_8$; member of the chlorite group) and minor serpentine (ideal formula: $Mg_3Si_2O_5(OH)_4$; detected polymorphs: lizardite and chrysotile). In magnesiochromite, Mg may be partially substituted by divalent Fe, and Cr may be partially substituted by Al and trivalent Fe, whereas serpentine may also show limited substitution of Mg for divalent Fe. The two independent XRD analyses of the fresh chromitite (before catalytic tests) are thus in perfect agreement. Chrysotile peaks disappear after both tests, whereas lizardite peaks only remain after Test N°3. After Test N°1 and Test N°3, amorphous silica is also observed.

The petrographic descriptions of the pulverized material observed by optical microscopy (S-7), as was used for the catalytic tests (Figure 3), as well as polished thin sections from the natural chromitite rock (Figure 4) confirm the XRD observations. The sample is a massive chromitite with a cataclastic texture and contains *ca.* 85−95 vol % magnesiochromite. Chlorite (frequently kämmererite ($(Mg,Cr)_6(OH)_8AlSi_3O_{10}$), the Cr-bearing variety of clinochlore), minor serpentine, calcite, and traces of millerite are secondary phases occurring interstitially among the chromite grains. Magnesiochromite crystals show local alterations to ferrichromite and Cr-bearing magnetite, which occur at thin rims around the crystals. Local garnet (mainly of hydrogrossular composition) fills the veins up to 50 μm thick or irregular areas (Figure 4). There are no major differences in the magnesiochromite or the formation of any new phase in the rock samples after Test N°1 and Test N°3. Rods and microfibers of amorphous silica were observed in both tested natural chromitite rocks, which is in line with the observations in the XRD2 patterns (Figure 3c,d). These fibers are probably residues from the catalytic test (S-7).

The External Surface State of the Chromitite. The XPS survey spectrum of the surface of the mineral grains of chromitite is presented in Section S-8. The XPS analysis (S-8) revealed an outer grain surface mostly composed, in decreasing order, of oxygen (O 1s: 534.1 eV, 56.9 at. %), magnesium (Mg 2s: 88.5 eV, 10.1 at. %), silicon (Si 2p: 102,6 eV, 6.5 at. %), aluminum (Al 2p: 73.8 eV, 4.2 at. %), chromium (Cr $2p_{3/2}$: 576.6 eV, 3.2 at. %), and iron (Fe $2p_{3/2}$: 709.9 eV, 2.3 at. %) atoms. Aliphatic carbon ($\underline{C}-(C,H)$, 284.8 eV, 12.2 at. %) and a low fraction of carbon bound to oxygen ($\underline{C}-O$: 286.3 eV, 2.3 at. %, $O-\underline{C}-O$ or $\underline{C}=O$: 288.0 eV, 1 at. %, $O=\underline{C}-O$: 289.4 eV, 0.8 at. %), which is the typical signature of adventitious carbon contamination inherent to XPS analysis, were also observed. No other elements were detected on the surface of the chromitite (with the detection limit being around 0.1 at. %). No evidence was observed for the presence of sulfates, sulfites, sulfides, fluorites, or nitrates. Similarly, no indication of peaks corresponding to platinum-group elements (PGE: Pt, Rh, Ru, Pd) was observed in the samples analyzed. A peak at 336 eV matches the position of the Pd 3d signal, but it should be rather assigned to Mg Auger, being a predominant element in the sample.[35] No other signals that could indicate the presence of Pd or Pt were found. The presence of any compounds containing Ni was also discarded. The most intense Rh 3d doublet falls at the same binding energies as the Mg Auger peaks (306 and 311 eV[13]), but since no signal corresponding to the Rh 3p doublet was detected (495 and 520 eV[13]), the presence of Rh is difficult to claim for the specific chromitite used in our study. A Ru content was also excluded since no asymmetry on the low-binding-energy side of the C 1s peak was observed, as would be expected from its $3d_{5/2}$ contribution (280 eV[13]) if Ru was present. After the catalytic test, no significant differences in binding energy and atomic concentration were observed.

DISCUSSION

The Abiotic Transformation of CO_2 in CH_4 on Natural Chromitite Rock. Presented in the literature for the first time is the experimental proof that a natural rock, a chromitite in this case, collected from an open-pit mine and without any previous pretreatment, can transform CO_2 in CH_4 via an abiotic process following the Sabatier reaction pathway. Transformation of CO_2 by hydrogen is realized, very probably, under the same environmental reaction conditions that occurred during methane formation in the natural setting of this chromitite sample, explaining the presence of host methane measured in a previous study.[6] Our results indicate that this transformation may be realized not only in the chromitite studied in this work, but very probably also in any other natural rock on Earth, that bears mineral phases that can act as catalysts. It would even be expected that in other natural rocks the transformation could be realized with higher efficacity. Our results prove that this transformation is realized following a heterogeneous catalytic process. The conclusion is that the natural rocks on Earth may contain catalytic sites to perform selectively the transformation of CO_2 and H_2 into methane, playing the role of a catalyst.

Even if during the early Earth formation, reaction conditions were different (probably more favorable: higher temperature and pressure), methanation takes place spontaneously, according to thermodynamics and catalysis kinetics. The catalytic rate of hydrogenation of CO_2 significantly would then be higher, which could be consistent with the large reserves of natural gas found in natural reservoirs on Earth. It can be suggested that other hydrocarbons (ethane, propane, butane, not detected in this study) could be probably formed via catalytic Fischer−Tropsch reactions. As the rate of methanation increases with the temperature and pressure, it is suggested that the extensive occurrence of this catalytic process in the porosity of various rock formations would not only explain the formation of large amounts of methane on Earth but also great amounts of water, which is the second product of CO_2 methanation and an important compound for the origin of life. It is important to underline that the presence of high amounts of CO_2 in all reservoirs of natural gas could be instead an indication of a Sabatier process and formation of abiotic methane. The abiotic process following the Sabatier reaction pathway is largely the most reasonable explanation of the gigantic amount of methane stored on Earth. This is explained by the fact that the catalytic process is highly performant and selective, can be realized in several and numerous natural places on Earth, is active in the catalytic transformation of CO_2 and H_2, in some cases on natural rocks containing very active catalytic sites, and can be performed during an extensive period without consumption of the natural rock. The sites perform the catalytic cycle for a very long time, in principle infinitely, except if a deactivation of the catalytic sites occurs. On the contrary, in serpentinization, which is cited often to explain the formation of methane on Earth, rocks are modified irreversibly due to the transformation needed to produce H_2, and then the amount of abiotic methane formed is limited by the amount of natural rock that can follow serpentinization. Even if this process can contribute to the formation of methane on Earth, its contribution is negligible compared with the methane formed by the heterogeneous catalytic process of CO_2 and H_2 in a natural rock, in the absence of serpentinization.

There is a consensus that the reduction of CO_2 to methane is important to account for the first stages in the emergence of life on Earth.[3,36,37] All these stages are processes that occurred under the conditions that existed on prebiotic Earth. We demonstrated experimentally the abiotic, catalytic activation of CO_2 in an unprocessed chromitite, at low temperature. The chromitite can activate CO_2, an otherwise very stable molecule, by catalytic dissociation forming the CO(ads), which is a highly reactive intermediate. It is strongly suggested that heterogeneous catalytic processes (owing to their very high reactivity and selectivity) on different rocks (having probably different origins and compositions) might have resulted in the formation (from CO(ads)) of complex organic molecules observed in Nature. Then the dissociation of CO_2 might be at the origin of the formation of precursors, which could be at the origin of the first block of life. It is then feasible that these catalytic processes are realized in any natural setting on Earth, which contain active catalytic sites to perform the hydrogenation of CO_2, giving precious arguments to explain and discuss the presence of life on Earth and maybe elsewhere in the Universe. In addition, CO_2 dissociation produces O(ads), which is a highly reactive oxidant. O(ads) can additionally contribute to the formation of further organic molecules (containing oxygen) and/or modulate the oxidation state of the catalytic sites of the occurring mineral phases. Our results using a natural chromitite rock as the catalyst open new challenges in the catalysis field not only regarding the origin of methane in the different natural settings on Earth but also regarding the formation of organic molecules on Earth and the formation of the precursors of the first block of life.

Attempts to Explain the Formation of Methane in the Presence of the Natural Chromitite Rock. Chromitite presents catalytic sites at its surface, which can transform gaseous CO_2 and H_2 in CH_4 and water via heterogeneous catalytic hydrogenation. As indicated previously,[9−22] pathways for the abiotic methanation of CO_2 have been principally validated in the presence of PGEs (platinum group elements)-containing phases (>0.5% in wt). Despite that PGEs were detected previously (in ppb amounts)[4,6] in a duplicate of the chromitite used in this study, in the present work, PGEs were not detected, at least on its surface. This conclusion is also supported by XPS analyses (S-8), where results show high surface sensitivity (a detection limit of around 0.1 at. % in the 5−10 outermost atomic layers).[38] The XPS technique is systematically used in heterogeneous catalysis to quantify the amount of active elements at the surface of metal-supported catalysts. XPS confirms the absence of PGEs in catalytically relevant amounts (at least in the 0.1 at. % range) on the surface of our samples. Consequently, the catalytic activity must be attributed to the mineral phases observed: magnesiochromite (with local alterations to ferrichromite and Cr-bearing magnetite), Cr-clinochlore, serpentine, lizardite, chrysotile, millerite, calcite, etc.

It is thus an important information that chromitite (in the absence of PGEs) could catalyze CO_2 hydrogenation into methane at atmospheric conditions. Previous studies have suggested that chromite, magnetite, Fe-Ni alloys, and iron- and chromium bearing minerals are active components of the mineral, which can catalyze the hydrogenation of CO_2 to methane.[6,7,23,24,26,30,31,33] Our results confirm previous studies and suggest additional mineral phases that could catalyze the hydrogenation, confirming that PGEs may not be the exclusive mineral-catalysts for methane formation. However, we must be careful in explaining the catalytic performances presented in the literature. Previous studies in catalysis point out that the catalytic activity observed in CO_2 methanation could be assigned either to a single crystal phase or to combination of two or more phases. Here, we do not have conclusive arguments to attribute the catalytic activity to an individual phase from the minerals observed in this study. We cannot exclude that several phases might synergistically or sequentially participate in the different steps of the methanation reaction. It is well accepted that different catalyst phases can interact under reaction conditions, leading to synergistic effects on the overall catalytic performance, as reported for several catalytic reactions (partial or total oxidation, oxidative dehydrogenation, and ammoxidation of hydrocarbons). Catalytic cooperation (migration of reactive surface atoms/molecules from one phase to the other, promotion of the formation/dissociation of reaction intermediates, structure−property relationships, metal function, operating conditions, etc.) can occur between separate phases and catalytic sites, with different but complementary properties and catalytic abilities, in close proximity.[39−43] The catalytic role of oxide phases in CO_2 methanation has been largely reported using synthetically prepared catalysts. For instance, high reaction rates have been attributed to Al_2O_3, ZnO, and MnO_x, CeO_2,[44] Fe-containing phases,[45,46] Co-Zr interfacial phases, oxygen vacancies of ZrO_2,[47] Zr-containing phase,[48] spinel-type $(Mg,Al)O_x$ matrix,[49] and γ-Al_2O_3-ZrO_2-TiO_2-CeO_2, Gd_2O_3, ZnO, TiO_2, and Nb_2O_5 multicomposite supports.[9−12,50] According to this evidence, the oxide and spinel phases detected in the natural chromitite rock should be capable of catalyzing the routes of CO_2 methanation, in the absence of catalytically relevant (in the sense defined above) amounts of PGEs. As said before, other natural rocks might present similar or different catalytic properties. The conclusion is that in natural rocks on Earth, the catalytic activity would be assigned to different oxide phases and to the content or not of PGEs.

Further Implications of the Abiotic Activation of CO_2. The results presented demonstrate that chromitite can activate a highly stable molecule such as CO_2. The role that the heterogeneous catalytic processes have in the activation of CO_2 and its transformation into methane has been well demonstrated in the literature using synthetic catalysts. Our results open a new area of research in order to investigate the nature of the phases and the active sites present in chromitite, which are responsible for the abiotic activation and hydrogenation of CO_2 and probably the formation of other molecules. As discussed above, research on synthetic catalysts shows that the dissociation and formation of the CO(ads) intermediate and O(ads) from CO_2 and H_2 via heterogeneous catalysis is the first step in the mechanism of abiotic formation of methane. Our work suggests that the same mechanism would be possible to occur in any rock on Earth if it presents the adequate catalytic sites. As discussed above, this step is important because it allows the transformation of inorganic C to organic C. As said above, formation of such an intermediate is critical to explain the origin of organic compounds on Earth. Hence, the formation of both methane and organic compounds in Nature depends on the activation of CO_2. It seems that our results allow going further in their implications. The literature has largely demonstrated that a synthetic catalyst (supported PGEs on oxides) can also activates, by heterogeneous catalysis, another stable molecule such as N_2, allowing ammonia synthesis ($N_2 + 3H_2 \leftrightarrow 2NH_3$, $\Delta H = -92, 4$ kJ/mol). The two first steps of this reaction are the activation of H_2 and N_2, forming NH as the intermediate, and then NH_3.[51,52] Then it can be suggested that a natural rock (not only natural chromitite rock) on Earth could also activate N_2. It is important to underline that it has been demonstrated in the literature that the same synthetic catalyst (ruthenium supported on alumina) is able to activate CO_2 and N_2, forming NH(ads) and adsorbed CO intermediates, respectively,[19,20,51,52] then giving the possibility to form these intermediates at the same place. It is suggested that the formation of these intermediates formed from CO_2 and N_2, as indicated above, might be at the base of the formation of organic compounds and amino acids observed in natural settings on Earth. Our results strongly support previous studies investigating hydrothermal areas (the Lost City hydrothermal field hosted on the Atlantis Massif). In these studies, extensive evidence of the presence of the nitrogen-containing amino acid tryptophan, in a context in which it was unlikely to have been produced by a biologically mediated process, has been presented. Data were obtained from three high-resolution techniques analyzing materials from natural rock samples in deeply serpentinized harzburgite (173.15 m below sea floor) where active serpentinization occurs. The presence of biomarkers was absolutely excluded confirming definitively that the process of formation of amino acid tryptophan is abiotic. It is suggested that catalytic Friedel−Crafts-type reactions may be responsible for the formation of abiotic aromatic amino acids during the hydrothermal alteration of oceanic peridotites being catalyzed by Fe-rich saponite.[53,54] Results obtained in the Lost City hydrothermal area strongly support the abiotic formation of amino acid in Nature and put in evidence the role of heterogeneous catalytic processes in its formation. Our results can be considered as a suggestion to understand the possible pathways of formation of amino acid in the Lost City hydrothermal field and probably in other geological setting on Earth.

Implications of the Catalytic Activity of Natural Rocks on CO_2 Mitigation. Current processes of carbon capture and storage (CCS) present major energetic, engineering, and contamination drawbacks, and the development of technologies is slowly progressing.[55,56] Actual CCS technologies can only help slow down the increase of global atmospheric CO_2 concentration, and more effective alternatives are urgently required.[57,58] Our work suggests, for the first time, that putting H_2 along with CO_2 into underground reservoirs for carbon sequestration can allow the formation of methane *in situ*, opening the possibility to recycle the CO_2, then contributing to protect the reserves of CH_4 on Earth. Presently, current processes of carbon capture and storage (CCS) can only help slow down the increase of global atmospheric CO_2 concentration, and then, CO_2 is stored in underground reservoirs forever. Results presented in this work may establish the basis for a new concept of simultaneous capture of carbon and hydrogen in adequate natural reservoirs, the carbon and hydrogen capture and storage (CHCS). We have shown that the complex combination of phases observed in the natural chromitite rock can catalyze the conversion of CO_2 into methane. The availability of oxides and other compounds, which could promote hydrogenation of CO_2[7,8,23−34] in natural geological cavities, gas and oil reservoirs, and shale gas reservoirs, has been reported, and therefore, methane can be formed in those storage sites. In addition, the eventual presence of small concentrations of PGEs could further considerably increase the rate of on-site methanation reaction. Green processes like photosynthesis, photocatalysis, water electrolysis, and biomass conversion could be used to produce the hydrogen required for the reaction. Clearly, the suitability of a given natural reservoir for CHCS applications will depend on several factors, including the composition and amount of injected gases, the hydrogen availability, the natural rock composition, the residence time of the gas in the reservoir, etc. Alternatively, the use of high amounts of inexpensive (low price) natural rocks to catalyze CO_2 methanation inside big industrial reactors can also be seriously envisaged. This is an exciting challenge for chemical engineering process development.

■ CONCLUSIONS

For the first time, an indisputable experimental proof of the (abiotic) formation of methane on chromitite, collected from an open mine and used, without any previous pretreatment, in the presence of gaseous CO_2 and H_2 under low temperature and atmospheric pressure, which are the expected atmospheric environmental conditions that existed on Earth's crust when methane was formed in Nature, is provided. Results confirm that methane can be produced in the absence of water in the reaction atmosphere. Methane is formed by a heterogeneous catalytic process following the hydrogenation of CO_2 (Sabatier reaction). Principally oxides and spinel phases and probably other minor phases detected in chromitite should be capable of catalyzing CO_2 methanation, in the absence of PGEs in catalytically relevant amounts. These results extend and strongly suggest the possibility that other natural rocks in Nature can transform, by heterogeneous catalytic abiotic processes, CO_2 to methane. Results suggest that methanation may have taken place spontaneously on Earth, which is consistent with the large reserves of natural gas found in natural cavities, and the presence of other hydrocarbons. Results suggest establishing the basis for a new concept of simultaneous capture of carbon and hydrogen in adequate natural reservoirs.

Understanding the origin of methane from CO_2 is also important because its formation would be related to the origin of life on Earth and maybe elsewhere in the Universe. Both processes seem indissociable. The reduction of CO_2 might correspond to the first step allowing the transition from CO_2 to CO (adsorbed) intermediate and to organic molecules, supporting the abiotic formation of organic compounds observed in natural settings on Earth. If the activation of N_2 is also considered, the formation of amino acids would be also explained.

■ OUTLOOK

During the last years, important contributions have allowed improvement in the understanding of possible pathways that might contribute to explaining the origin of life.[59−62] Experiments in the laboratory have been done to verify different theories that might explain chemical stages that could drive the formation of the first block of life. Certainly, these studies are necessary to understand mechanisms allowing the synthesis of complex molecules. However, life originated in Nature, in places where all conditions allowing these transformations were accessible. Life originated from, apparently, single organic compounds, which were transformed to complex organic molecules and amino acids having precise structure and chirality properties. Some studies have been performed investigating the synthesis of organic molecules but using *in vitro* strategies. Then the urgency now is to identify the catalytic sites present in natural rocks, which might have participated in life creation processes. This work seems to give important insight to advance in this direction. It has been underlined that the first block of life has been formed spontaneously from the compounds present in the atmosphere existing in contact with the natural rock, namely, in the presence of CO_2(g), N_2(g), H_2 (g), O_2(g), and P (or phosphate). Our results demonstrate that very stable molecules (CO_2, N_2) and H_2 are activated by heterogeneous catalysis forming the adsorbed (and very reactive) intermediates (CO, O, NH, H). An important consequence of the activation of CO_2 is also the formation of O(ads), which is a strong oxidant, more active than O_2. On the other hand, catalysis can allow the formation of C−N, C−O, and C−P bonds.[63] It would be expected that heterogeneous catalysis plays also a role in the activation of P or phosphate and in the formation of complex organic molecules and amino acids. Then to advance this, it is necessary to study further reactions using these intermediates as reactants. These reactions must be realized with a very high selectivity considering all the possibilities of transformation of reactants, intermediates, and products predicted by thermodynamics. The participation of heterogeneous catalysis in these transformations is probably the unique possibility to maintain a high selectivity in these processes, avoiding nondesired reactions. Our work seems to give, for the first time, arguments suggesting that heterogeneous catalytic processes play an important role in the activation of the gaseous molecules present in the prebiotic chemistry period and would be involved in the origin of the first blocks of life on Earth. A multidisciplinary and closed contribution of scientists with experience in different fields (chemists, physicians, biologists, biochemists, engineers, etc.) is necessary to go further ahead.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsearthspacechem.1c00046.

> Materials and methods: S-1: Collection of natural chromitite rock. S-2: Catalytic activity measurements. Supplementary materials: S-3: Mass transfer limitations. S-4: ICP-AES analysis. S-5: X-ray fluorescence (XRF) analysis. S-6: X-ray diffraction (XRD). S-7: Petrographic descriptions: reflected light polarizing (optical) microscopy and SEM. S-8: X-ray photoelectron spectroscopy (XPS) (PDF)

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All authors have given approval to the final version of the manuscript. C.F. performed the reaction tests, catalytic activity analysis, and preliminary XPS measurements, wrote the corresponding sections of the manuscript, and contributed in writing and editing the final text. E.I. collected the rock samples, performed the XRD2 and SEM analyses, interpreted the results, and contributed to rock characterization and analysis of results, as well as to manuscript writing. P.E. performed XPS measurements and analysis of results and wrote the corresponding section of the manuscript. I.M.-T. performed XRD1 measurements and analysis of results. F.D. contributed to performing XRD1 and XPS measurements. E.M.G. coordinated the characterization measurements, compiled and correlated the data obtained, and contributed to manuscript writing. B.T. performed the XRD2 and SEM analyses, interpreted the results, and contributed to rock characterization and analysis of results, as well as to manuscript writing. P.R. carried out the design and the direction of the research and the project and contributed to the experimental data analysis, interpretation of results, and to manuscript writing.

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Notes

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